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INFLUENCE OF PHOSPHORUS UPON THE MICRO-STRUCTURE AND HARDNESS OF LOW-CARBON, OPEN-HEARTH STEELS

By Edward C. Groesbeck

ABSTRACT

In this investigation, undertaken with the object of throwing additional light on the rôle played by phosphorus upon the properties of low-carbon, open-hearth steels which are often used in the manufacture of products where severe cold working is employed during fabrication, no clear relationship could be established between the phosphorus content, varying within the range 0.008 to 0.115 per cent, which marks the usual limits in plain carbon steels, and the microstructure and hardness as developed in two series of specimens, one of basic open-hearth steel and the other of acid open-hearth steel, by a series of different heat treatments, because of the marked irregularity in the distribution and grain size of the ferrite and pearlite grains found present in many of the specimens. This irregularity was traced, by means of the microstructure as developed by etching, to the nonuniform distribution of the phosphorus. A cellularlike structure formed in conjunction with the microstructure normal to these steels was studied and relationship between this unusual structure and the distribution of phosphorus was established.

Because of the very limited amount of material available for this investigation it was not possible to extend the scope of the work beyond the study of the microstructure and hardness of the steels in question.

CONTENTS

I. INTRODUCTION

In connection with an investigation made several years ago into the effect of varying phosphorus content upon the endurance qualities of low-carbon steel when severely cold worked, as in stamping, drawing, pressing, upsetting, and bending, Dr. J. S. Unger [1] prepared two series of ingots, one of basic open-hearth steel and the other of acid open-hearth steel, all having the same general composition, but with the phosphorus content varying from 0.008 to 0.11 per cent, and which comprises the range of phosphorus content usually found in acid open-hearth and acid Bessemer steel. These steel ingots were rolled down into the usual billets, slabs, and sheet bar preparatory to the formation by cold work of the various products upon which the tests were made. These steels were given no other than the customary heat treatment accorded ordinary soft steels during the process of fabrication. Through Dr. Unger's kindness, a small quantity of material in the form of 1-inch rounds from the two series of ingots was made available for this study.

There appears to be scant information of a systematic nature in the published literature with regard to the influence of varying amounts of phosphorus, especially within the limits usually found for this element in open-hearth and Bessemer steel, upon the microstructure and physical properties of low-carbon steel as developed by heat treatment. D'Amico published in 1913 [2] the results of an investigation carried out on the microstructure, hardness, mechanical, and magnetic properties as developed by heat treatment in a series of 12 low-carbon steels, made by the electric process, to which phosphorus had been added, so that the resulting phosphorus content varied from 0.012 to 1.242 per cent. Only two of his steels come within the range of phosphorus content covered in this investigation. Dr. Unger [3] stated that in his investigation the effect of heat treatment was not studied, inasmuch as soft steels are rarely heat treated, though he made a few tensile and other tests on some heat-treated bars.

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[1] J. S. Unger, Proceedings Amer. Iron and Steel Inst., 1918, pp. 172–193; also Iron Age, **101**, p. 1538; June 13, 1918.

[2] E. D'Amico, "Uber den einfluss des phosphors auf die eigenschaften des flusseisens," Ferrum, **10**. pp. 289–304.

[3] See footnote 1.

II. AIM OF INVESTIGATION

The scope of this investigation, undertaken with the hope of throwing additional light on the rôle played by phosphorus upon the properties of the steels in question or, at least, of the ordinary low-carbon steels which are used for the manufacture of products where severe cold working is employed during fabrication, was confined to the relationship between the phosphorus content, as present within the limits 0.008 to 0.115 per cent, and the microstructure and hardness as developed by a series of heat treatments and also the distribution of the phosphorus in the steel as revealed by metallographic etching.

III. PREPARATION OF MATERIAL

1. MATERIAL

The steels used in this investigation were of the following general chemical composition: Carbon, 0.12 per cent; manganese, 0.36 per cent; silicon, 0.020 to 0.022 per cent; sulphur, 0.036 to 0.037 per cent; copper, 0.012 to 0.014 per cent; and phosphorus as below:

Basic open-hearth series		Acid open-hearth series	
	Per cent		Per cent
Steel A.........................	0. 008		
Steel B.........................	.030	Steel BB........................	0. 032
Steel C.........................	.052	Steel CC........................	.058
Steel D.........................	.080	Steel DD........................	.085
Steel E.........................	.110	Steel EE........................	.115

The limited amount of material made available for this study necessitated the use of small samples. Transverse slices one-fourth inch thick were cut from the 1-inch rounds and these slices in turn radially into quarters. Each specimen thus presented a face approximately a quadrant of a circle of one-half inch radius for microscopic examination and hardness determination.

The nine specimens, one from each of the steels in both the B. O. H. and A. O. H. series for each heating, were fastened three in a row to a piece of rather coarse iron wire gauze, which was wrapped around the pyrometer tube at the closed end in such a way that the three rows of specimens were placed approximately equidistant around the outer circumference of and in contact with the pyrometer tube and also so that the hot junction of the chromel-alumel thermocouple, used in conjunction with a millivoltmeter, was approximately centrally located within the cluster of the nine specimens.

2. APPARATUS

All but one of the heatings were carried out in a horizontal tubular nichrome-wound electric furnace, provided with an iron pipe 2¾ inches inside diameter and 27 inches long, over which was slipped a fairly snug fitting alundum cylinder 24 inches long and around which the heating element was wound. The equalization of the temperature within the hotter part of the iron-pipe furnace tube was aided by means of baffle plates, and the specimens to be heated were placed within the portion of the furnace tube found by trial to have the flattest thermal gradient, namely, about 5° C over a distance of 2½ inches. Boats filled with ground charcoal were placed within the furnace tube near both ends in order to counteract the decarburizing conditions as far as practicable. In the lead-bath heating, which was carried out in a gas-fired, lead-bath furnace, the specimens were placed around the nichrome pyrometer protection tube at the closed end in a similar manner as in the other heatings, and this tube was placed in such a position that the specimens were approximately in the center of the molten lead bath, which was about 6½ inches in diameter and 11 inches deep.

3. EXPERIMENTAL PROCEDURE

A series of six heat treatments was made, in which the rate of cooling from the maximum temperature, 900° C, was so regulated that the cooling through the 750 to 600° C range occupied the following periods of time: Four hours, 2 hours, 1 hour, 30 minutes, 15 minutes, and 5 minutes. In all cases the cooling from 900 to 750° C was so controlled that the rate of cooling in this range would correspond as closely as practicable to that followed through the 750 to 600° C range, which was chosen as that in which the formation and the break-up of the lamellar pearlite into "granular" pearlite occurred in order to note whatever influence the phosphorus content might have on this tendency. In the lead-bath heating (HT-7) the gas and air were shut off entirely soon after the maximum temperature, 900° C, was reached, and the cooling of the bath and specimens was allowed to proceed uninterruptedly in the furnace until the temperature of the bath had reached 500° C when the specimens were taken out and allowed to cool in the air.

Fig. 1 shows graphically the heating and cooling curves for all the seven heatings carried out.
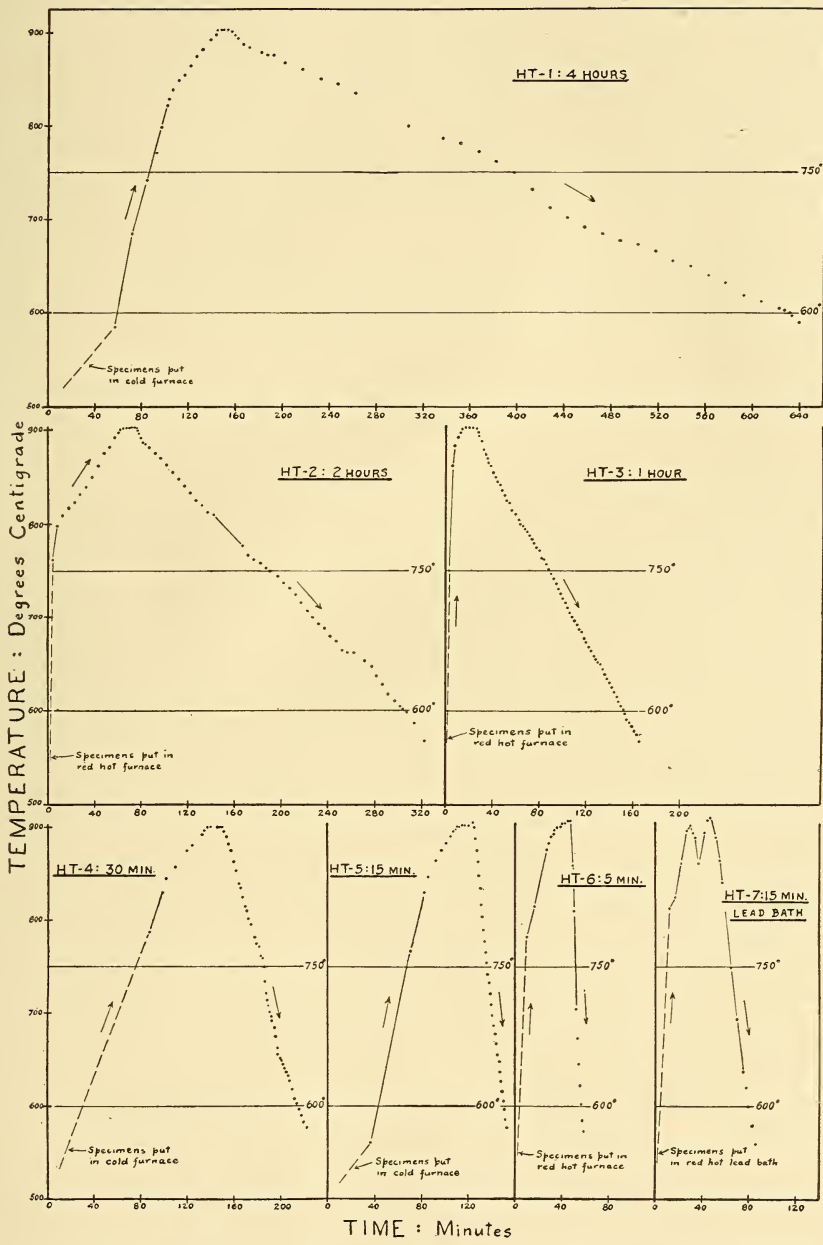
FIG. 1.—*Heating and cooling diagrams for the series of heat treatments carried out*

See Table 1 for the lengths of time covered by the various stages of the heatings and coolings.   The times given in the title for each of the diagrams refer to that taken in cooling down through the 750–600° C range.

In Table 1 are given the periods of time occupied by the different stages of the heatings and coolings.

TABLE 1.—Heat Treatment—Times of Heating and Cooling

Laboratory number	Desired rate of cooling through 750–600° C	Condition of furnace on insertion of specimens	Heating interval		Cooling interval	
			To 900° C	At 900° C	900–750° C	750–600° C
	Minutes		Minutes	Minutes	Minutes	Minutes
HT–1.....................	240	Cold.......................	145	12	241	234
HT–2.....................	120	Red hot...................	61	15	109	116
HT–3.....................	60	.....do...................	14	12	61	$63\frac{1}{2}$
HT–4.....................	30	Cold.....................	137	12	35	$29\frac{5}{12}$
HT–5.....................	15	Hot.......................	110	15	$11\frac{1}{3}$	$14\frac{1}{3}$
HT–6.....................	5	Red hot [a]...............	35	14±	2±	$6\frac{1}{6}$
HT–7.....................	[b] 15	Red hot...................	42	[c] 10±	16±	15

[a] The pipe container with the specimens was put back into the furnace immediately following a heating to 900° C and cooling down below 500° C, as the cooling through the 750 to 600° C range was found to have been too fast.

[b] Lead bath.

[c] During the holding at 900° C, the air blast stopped for a moment, so the temperature fell from 900° C, where it had been for about four minutes, down to 862° C, and it was raised again to 900° C, remaining at or above that temperature for six minutes more.

In the HT–5, 15 minutes, and HT–6, 5 minutes, heat treatments, an iron pipe $1\frac{1}{2}$ inches in diameter and 10 inches long overall, with iron caps screwed on at both ends, was used as a container for the specimens. Iron rods were fastened lengthwise to the container at the bottom in order to give a clearance between the furnace-tube wall at the bottom and the caps at both ends of the container and to facilitate the passage of air underneath in the 15-minute cooling. The fused silica pyrometer tube was inserted through a hole in the cap at one end of the container. The container was so situated in the furnace tube that the cluster of specimens placed in the center of the container would lie within the zone where the thermal gradient was flattest.

In the HT–5, 15 minutes run, the cooling of the pipe container and specimens was effected by means of a stream of air (laboratory table air blast) introduced through silica tubes placed through both ends of the furnace tube, one directed at the upper edge of one end and the other at the lower edge of the opposite end of the container.

In the HT–6, 5 minutes run, the pipe container was at the start of the cooling shoved out of the furnace tube into a 12-inch long and 3-inch diameter alundum tube surrounded by pipe insulation covering that had been preheated to a couple of hundred degrees

centigrade above room temperature and both open ends of the alundum tube were then immediately plugged up in order to check the outflow of the heat. In this manner the cooling of the specimens through the 750 to 600° C range was so regulated as to take about five minutes.

IV. MICROSTRUCTURE

In the grinding of the heat-treated specimens for microscopic examination and hardness determination ample allowance was made for the decarburization produced during heat treatment, and the extent of which was ascertained by measuring the thickness of the decarburized layer at one edge of a copper-plated and rather heavily ground specimen that had been given the longest heating (HT–1) carried out in the series of heatings.

1. GENERAL STRUCTURE

It was noted from a study of micrographs, taken of all the heat-treated specimens at near each corner of the quadrant-shaped specimen, that there is a marked irregularity in the distribution and size of both the ferrite grains and pearlite kernels in many of the specimens, especially in the A. O. H. steels as compared with that for the B. O. H. steels, and that there is no definite relation between the occurrence of this irregularity of structure and the phosphorus content and heat treatment.

Figs. 2, 3, 4, and 5, which were selected from the steels having the minimum and maximum phosphorus content (the 0.008 per cent phosphorus B. O. H. steel possessed a similar structure and grain size to that of the 0.030 per cent phosphorus B. O. H. steel for all the seven heatings) and were cooled through the 750 to 600° C range in 4 hours, 30 minutes, 5 minutes, and in the lead bath, illustrate in a general way the structure as developed in the different steels by the various heat treatments tried. For the steels of intermediate phosphorus content and cooled at the other rates tried, the structure is similar to that shown for the higher or lower phosphorus content and the more slowly or quickly cooled steels. There were several cases in which there was a marked deviation from the general structure as outlined above, and these cases are indicated in Table 2, where there is a large increase in the average grain area, as compared with that for the more slowly or quickly cooled specimens for the same steel.

It should be borne in mind that the grain size, as shown in Figs. 2 to 5, represents the effect, or rather the grain growth,

FIG. 2.—*Microstructure of low-carbon basic open-hearth steel containing 0.030 per cent phosphorus.* ×100

Heated to 900° C and cooled through 750-600° C range in the periods of time as indicated. Etching reagent, 5 per cent alcoholic solution of picric acid.

FIG. 3.—*Microstructure of low-carbon acid open-hearth steel containing 0.032 per cent phosphorus.* ×*100*

Heated to 900° C and cooled through 750–600° C range in the periods of time as indicated. Etching reagent, 5 per cent alcoholic solution of picric acid.

FIG. 4.—*Microstructure of low-carbon basic open-hearth steel containing 0.110 per cent phosphorus.* ×100

Heated to 900° C and cooled through 750–600° C range in the periods of time as indicated. Etching reagent, 5 per cent alcoholic solution of picric acid.
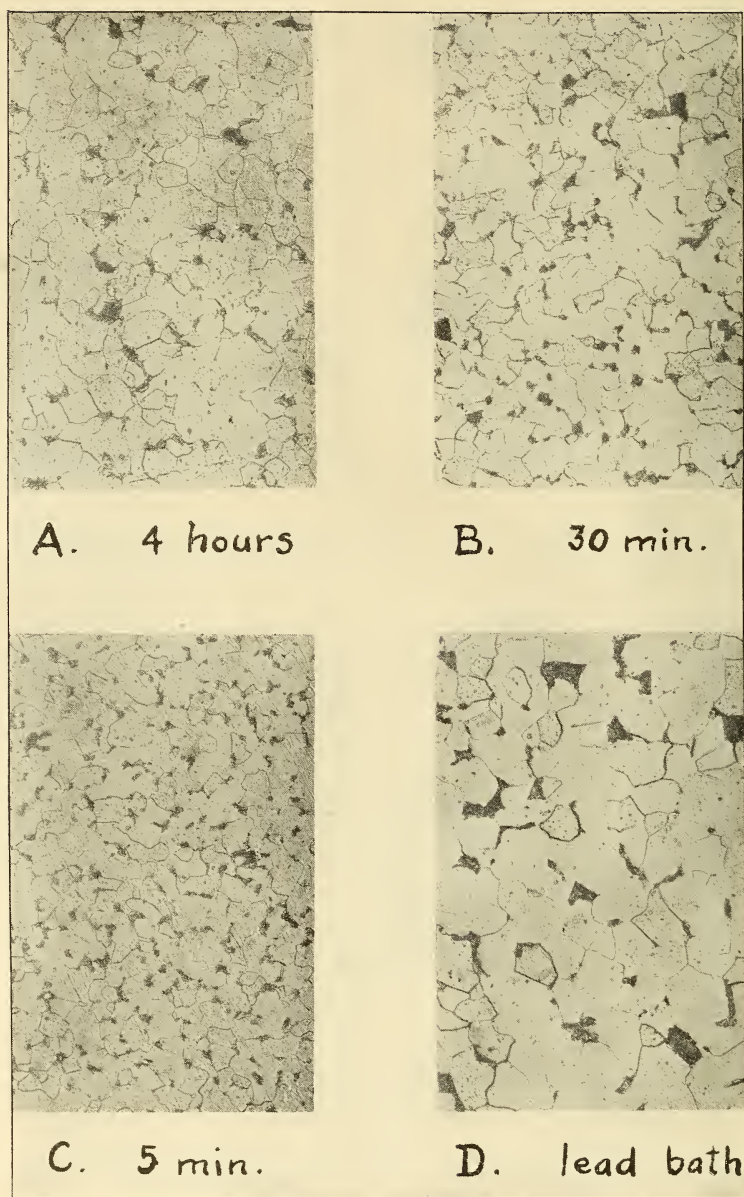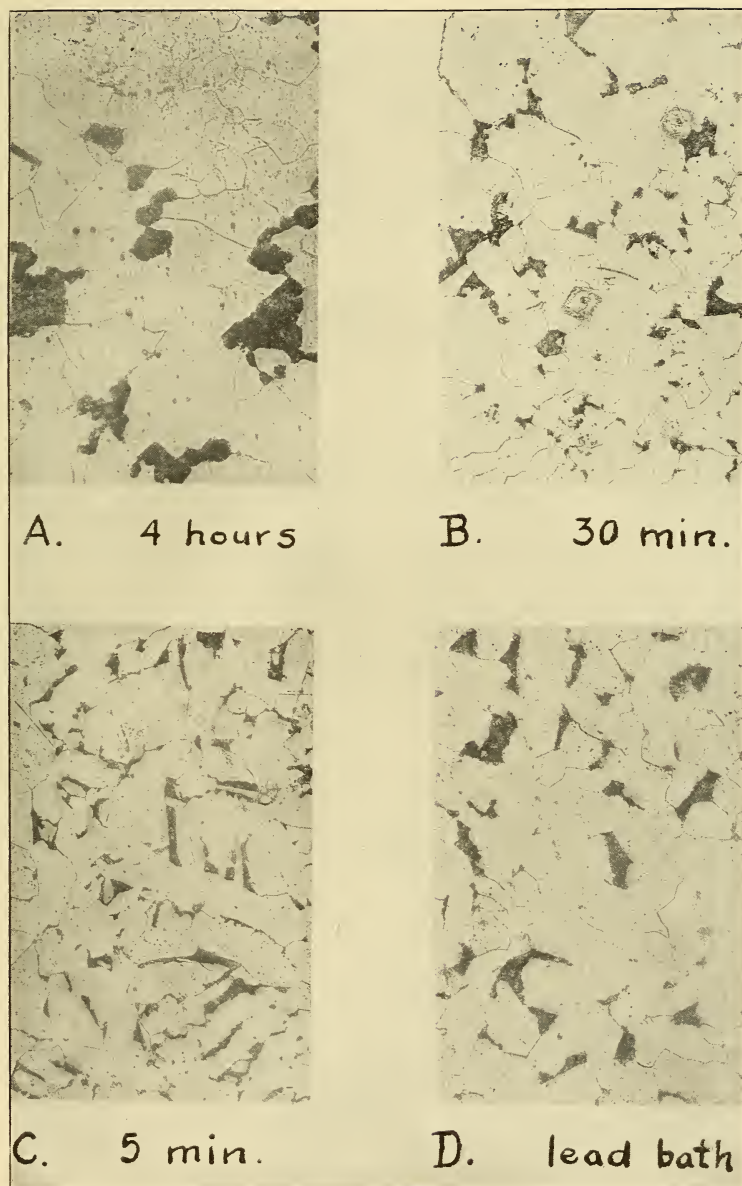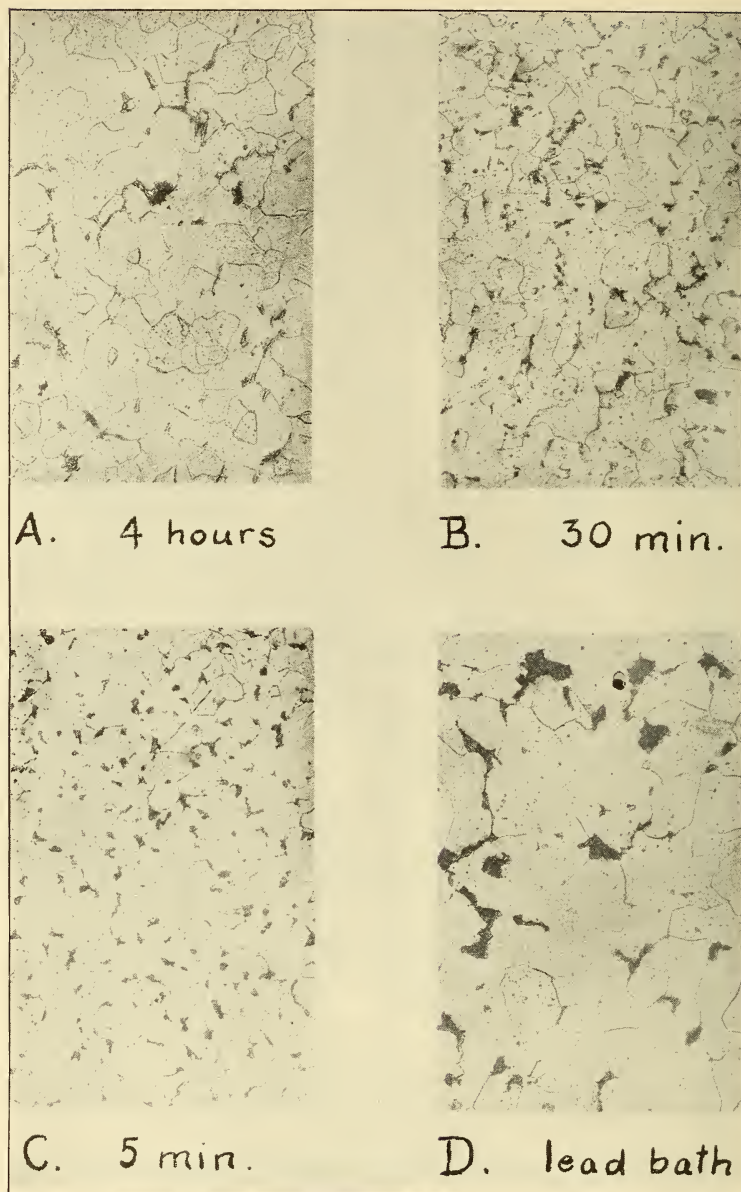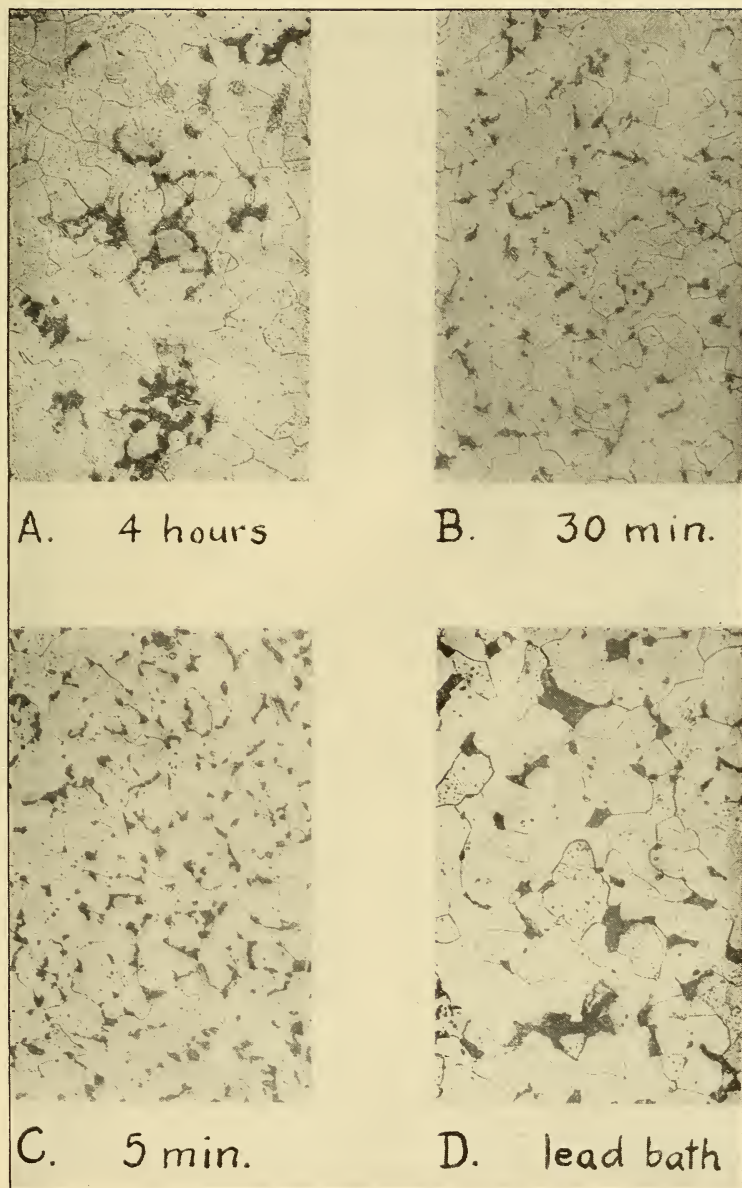
FIG. 5.—*Microstructure of low-carbon acid open-hearth steel containing 0.115 per cent phosphorus.* ×100

Heated to 900° C and cooled through 750–600° C range in the periods of time as indicated. Etching reagent, 5 per cent alcoholic solution of picric acid.

produced during the interval of time above the A_3 point occupied by the specimens in the course of the heat treatment. The data in the table given below are quite in agreement with what might be expected as to the relative grain size developed in the various specimens during the different periods of heating and cooling above the A_3 point (assuming Ac_3 for the two series of steels used in this investigation to be at 860° C) with the exception of the HT–7, lead-bath specimens, which show a marked increase in grain size even to a greater extent in all cases but one than in the case of the most slowly cooled series of specimens (HT–1, 4 hours). No satisfactory explanation can be offered as to the reason why the much shorter time of interval (33 minutes) above 860° C should develop an appreciably larger grain size in the HT–7, lead-bath specimens, than that developed in the specimens which were more slowly heated and cooled in the electric furnace (HT–1, 4 hours, and HT–4, 30 minutes).

Heat treatment (see Table 1)	Time of interval above 860° C	Average grain size in μ^2 (Table 2)			
		B. O. H. per cent P		A. O. H. per cent P	
		0.030	0.110	0.032	0.115
	Minutes				
HT-1, 4 hours.............................	96	911	1075	3304	1161
HT-4, 30 minutes......................	50	767	1019	1728	924
HT-6, 5 minutes.........................	26	589	714	1329	990
HT-7, 15 minutes (lead bath).................	33	1736	2111	1682	1713

2. IRREGULARITY OF STRUCTURE

In several of the specimens there were found present in the structure large areas (amounting in extent to about 15 per cent of the area of the microscopic field) which were quite free from pearlite and had small to very large ferrite grains, as Figs. 6 and 7 will show. These carbonless areas appear to be due to the presence of a greater concentration of phosphorus, arising from non-uniformity in the distribution of the phosphorus in the steel which will be discussed in a later section of this article.

3. RELATION BETWEEN GRAIN SIZE AND PHOSPHORUS CONTENT

In Table 2 are given the results of the grain-size determination made of all the heat-treated specimens. The planimetric method of grain-size determination as modified and described by Jeffries[4]

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[4] Z. Jeffries, Trans. Am. Inst, Min, Engrs., 54, p. 594; 1916. Also Met. and Chem. Eng., 18, p. 185; 1918.
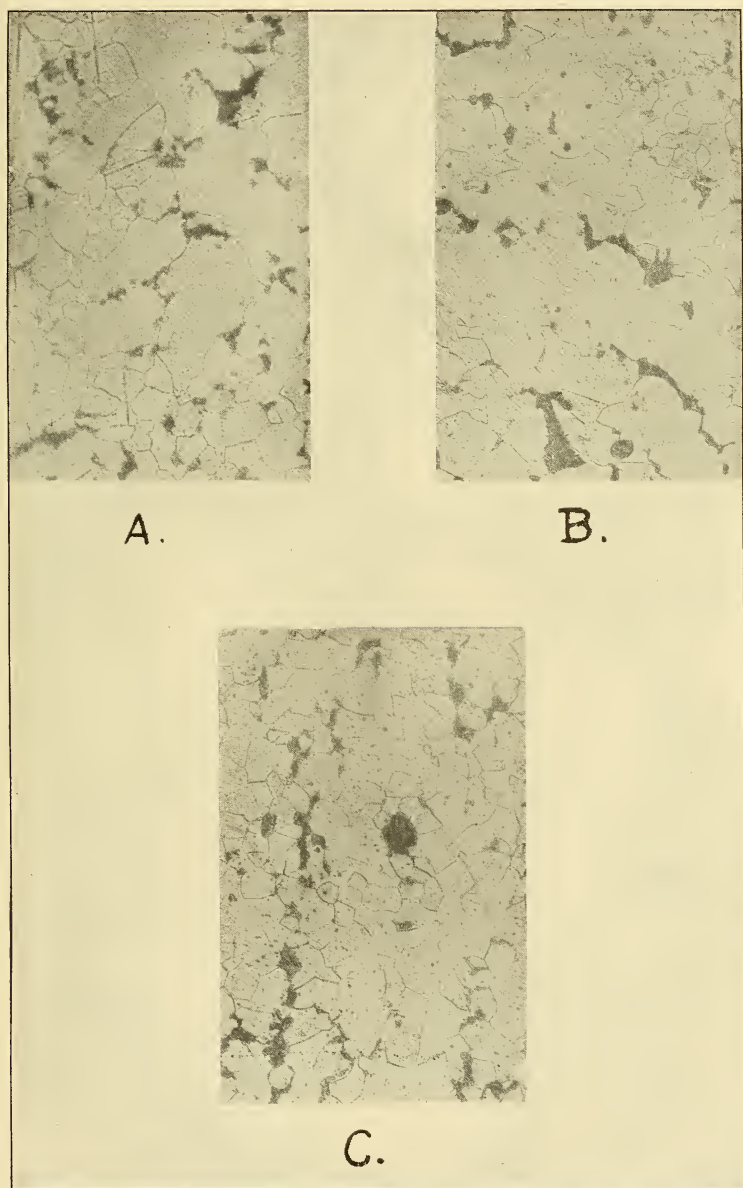
FIG. 6.—*Typical examples of irregularity in microstructure as found present in many of the specimens.* ×*100*

All the specimens were heated to 900° C and cooled through the 750–600° C range in the periods of time as indicated below. Etching reagent, 5 per cent alcoholic solution of picric acid. A—Low-carbon basic open-hearth steel containing 0.052 per cent phosphorus—30 minutes; B—Low-carbon basic open-hearth steel containing 0.110 per cent phosphorus—1 hour; C—Low-carbon acid open-hearth steel containing 0.115 per cent phosphorus—2 hours.
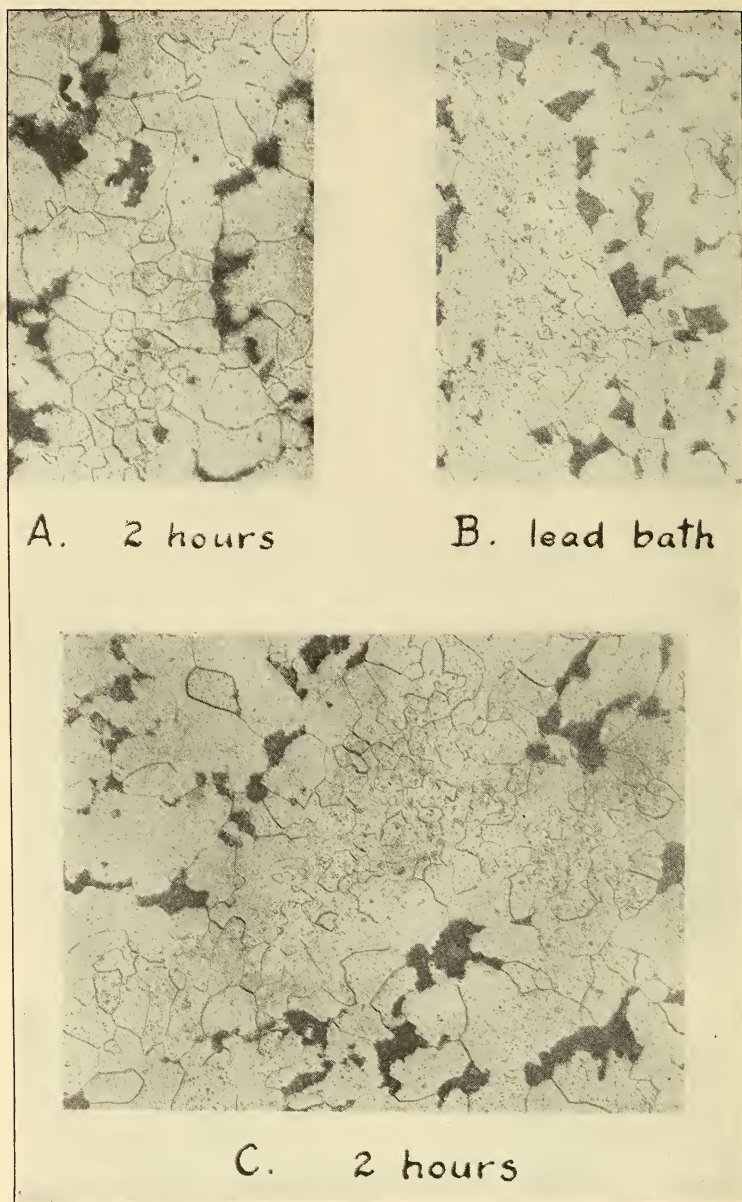
FIG. 7.—*Microstructure of low-carbon acid open-hearth steel containing 0.032 per cent phosphorus.* ×100

Heated to 900° C and cooled through 750-600° range in the periods of time as indicated. C is of the same specimen as A, but taken at a different spot. Shows carbonless areas as found in a few of the specimens, though particularly in specimens from this steel. Etching reagent, 5 per cent alcoholic solution of picric acid.

was followed. The pearlite kernels were counted together with the ferrite grains in determining the average area of the grains, the pearlite kernel being assumed as a grain. In comparing the average size of the pearlite kernels with that of the ferrite grains, the pearlite kernels appear, as estimated by the eye, to be about one-quarter in size of that of the ferrite grains for the quickly cooled sets of specimens (15 minutes and 5 minutes—B. O. H. and A. O. H.), one-half in size for some of the more slowly cooled sets (4 hours, 2 hours, 1 hour, 30 minutes, lead bath—B. O. H. and 30 minutes, lead bath—A. O. H.) and one-half to full size in the remaining slowly cooled sets (four hours, two hours, one hour—A. O. H.). The ratio of the number of ferrite grains to pearlite kernels (F:P) has also been determined, and the results are given in Table 2. There appears to be a well-defined and marked decrease in this ratio in the relatively quickly cooled specimens (15 minutes, 5 minutes, and lead bath) as compared with that prevailing for the more slowly cooled samples, and this is quite in accordance with what might be expected when one considers the opportunities the carbon has for being precipitated out of solid solution or austenite and the resulting pearlite masses to coalesce into larger masses during the cooling from 900° C, or above A_3, down through the transformation range. No relationship is seen to exist, however, between the ratio of ferrite grains to pearlite kernels (F:P) and the phosphorus content.

TABLE 2.—Average Area of Grain Section of Ferrite and Pearlite, in μ^2

The pearlite kernels are included together with the ferrite grains in the grain count, and the ratio of ferrite grains to pearlite kernels (F:P) is given in the table below. Each value in this table is the average of three determinations made of each specimen, one at each corner of the quadr[a]nt-shaped specimen]

| Phosphorus content, per cent | Grain section, when cooled through 750–600° C range in— | | | | | | | | | | | | | |
| | 4 hours | | 2 hours | | 1 hour | | 30 minutes | | 15 minutes | | 5 minutes | | Lead bath, 15 minutes | |
	Average grain area	F:P	Average grain area	F:P	Average grain area	F:P	Average grain area	F:P	Average grain area	F:P	Average grain area	F:P	Average grain area	F:P
B. O. H. 0.008	914	6.5	803	8.3	893	4.6	863	4.4	637	4.2	531	3.0	1683	2.5
B. O. H. 0.030	911	5.9	851	6.8	941	6.5	767	4.3	754	3.3	589	3.0	1736	4.2
B. O. H. 0.052	1103	6.4	1716	4.6	1080	5.3	1049	4.0	858	3.5	1137	4.4	1615	2.5
B. O. H. 0.080	806	8.7	768	8.8	1635	5.0	798	5.6	793	3.8	578	2.9	1803	2.8
B. O. H. 0.110	1075	10.6	948	9.5	976	5.4	1019	4.6	892	3.1	714	2.8	2111	3.6
A. O. H. 0.032	3304	5.8	2627	4.9	2230	2.6	1728	2.6	1532	2.0	1329	1.6	1682	3.6
A. O. H. 0.058	867	5.9	852	5.4	1328	5.6	704	4.7	778	2.7	830	2.4	1636	3.4
A. O. H. 0.085	1994	6.8	1814	5.0	1811	3.7	1052	4.1	1017	2.5	1384	1.8	1757	2.8
A. O. H. 0.115	1161	7.7	1154	5.7	1635	3.9	924	4.3	1029	2.7	990	2.0	1713	2.8

Because of the irregularity in the grain-size results, which was evidently due to the nonuniform distribution of the phosphorus in the steels, no definite conclusions could be drawn as to the relationship between the grain size and phosphorus content and also the effect of various rates of heating and cooling followed in the series of heat treatments.

4. EFFECT OF RATE OF COOLING UPON THE PEARLITIC STRUCTURE

With respect to the effect of the rate of cooling through the 750 to 600° C range, the divorcing of pearlite had progressed to some extent in the more slowly cooled specimens (4 hours, 2 hours, 1 hour, and 30 minutes, especially in the steels with higher phosphorus content) and this divorcing and the coalescing of the liberated cementite appear to have been more pronounced in the B. O. H. steel specimens than in the A. O. H. ones. However, there appears to be no well-defined relation between the degree of divorcing developed and the phosphorus content, within the limits 0.008 to 0.115 per cent phosphorus.

The undivorced pearlite was found to be mainly in the sorbitic and sublamellar [5] conditions for both B. O. H. and A. O. H. series of specimens, though in the more slowly cooled specimens (four hours, two hours, and one hour) there was a considerable quantity of fine lamellar pearlite present.

V. HARDNESS

1. EXPERIMENTAL DATA

Both the Shore and Brinell hardness values were determined, and the results are given in Table 3. In the Brinell test the specimens were too small and thin to permit the use of a 3000 kg load without distortion arising from the indentation of the specimen, so a 500 kg load was used instead with entire satisfaction.

2. ANALYSIS OF RESULTS

(a) SHORE.—The results, which are rather irregular, show no well-defined relation between the hardness and the phosphorus content and also the rate of cooling through the 750 to 600° C range. The range between the minimum and maximum individual values was 12.0 to 21.0 = 9.0, and 70 per cent of the individual values lay between the limits 17.0 and 19.0.

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[5] H. M. Howe and A. G. Levy, "Notes on pearlite," Jour. Iron and Steel Inst., 94, p. 220; 1916, II.

TABLE 3.—Brinell and Scleroscope Hardness

[Brinell: 500 kg load applied for 30 seconds, using a 10 mm diameter ball. Shore: Self-registering scleroscope with universal hammer. Average of seven determinations for each specimen]

| Phosphorus content, per cent | Hardness for specimens cooled through 750–600° C range for— | | | | | | | | | | | | | |
| | 4 hours | | 2 hours | | 1 hour | | 30 minutes | | 15 minutes | | 5 minutes | | Lead bath, 15 minutes | |
	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore	Brinell	Shore
B. O. H. 0.008	56	17.9	55	18.0	56	18.6	59	19.1	58	17.4	61	18.9	60	18.6
B. O. H. 0.030	58	17.1	61	16.8	a65	18.5	63	19.1	62	17.5	65	19.1	63	15.8
B. O. H. 0.052	64	14.9	65	16.6	61	18.1	68	18.1	64	17.4	62	16.9	68	14.8
B. O. H. 0.080	65	16.5	68	16.8	67	17.2	67	17.8	70	18.0	68	18.7	73	17.3
B. O. H. 0.110	63	17.9	65	18.5	70	17.9	67	20.3	68	18.6	72	19.1	73	17.5
A. O. H. 0.032	60	16.4	69	17.2	63	17.1	68	16.3	68	17.9	69	18.4	70	17.8
A. O. H. 0.058	69	17.1	69	18.1	73	17.7	73	18.9	74	17.3	67	19.3	74	18.1
A. O. H. 0.085	70	18.9	70	18.0	68	18.8	74	19.4	74	18.8	73	19.0	73	19.3
A. O. H. 0.115	74	18.3	65	17.1	72	17.4	73	18.3	73	17.9	74	18.8	73	17.6

a Load of 3000 kg used (specimen too small to prevent distortion at this load)

(*b*) BRINELL.—A more satisfactory relationship was obtained between the hardness and phosphorus content. In all of the seven differently heated sets of specimens there is a small but definite increase in hardness, as the phosphorus content is raised from 0.008 to 0.080 per cent in the B. O. H. series, though the hardness remains practically stationary as the phosphorus content is increased to 0.110 per cent, excepting in the one hour and five minute sets, where the increase in hardness continues. In the A. O. H. series the results are rather erratic, though in a general way the hardness increases a little as the phosphorus content is increased from 0.032 to 0.058 per cent and then remains practically stationary as the phosphorus is increased to 0.115 per cent. In the four-hour set the increase in hardness is practically continuous as the phosphorus content is increased from 0.032 to 0.115 per cent. In most of the sets of heat-treated specimens, both B. O. H. and A. O. H., the increase in hardness is quite in agreement with the rate of increase as indicated in the statement by Stead [6] that the Brinell hardness of saturated solid solution of iron phosphide in iron increases with the phosphorus content by about 1.3 points for each 0.01 per cent phosphorus. D'Amico [7] reports an increase of hardness by about 12 Brinell hardness numbers for each 0.1 per cent phosphorus.

No well-defined relationship could be established between the hardness and the rate of cooling through the 750 to 600° C range, though the more slowly cooled specimens (four hours, two hours, and one hour, B. O. H. and A. O. H.) were, in general, a little softer than the more quickly cooled ones.

VI. DISTRIBUTION OF PHOSPHORUS

1. STEELS WITH LOWER PHOSPHORUS CONTENT

As stated in Section IV (2), there were met with, during the microscopic examination of the entire series of specimens prepared for this investigation, a number of specimens in which large carbonless or free from pearlite areas and abnormally large ferrite grains were found present in portions of the microsection. These irregularities in structure were attributed to a nonuniform distribution of the phosphorus, there being a greater concentration of this element present in these carbonless and

[6] Stead, "Some of the ternary alloys of iron, carbon, and phosphorus," Jour. Soc. Chem. Ind., 33, p. 174; 1914.
[7] See footnote 2.

large ferrite-grains areas than in the surrounding metal. In addition, in several of these large carbonless areas there was noticed an unusual structure distributed throughout the cluster of ferrite grains and which appeared to stand out in relief as viewed through the microscope using vertical illumination.[8] This structure may be seen in Figs. 8, *a*, and 9, *d*, and it was clearly seen when the rest of the microscopic field was in focus. On closer examination this relief structure was found to form a part of a net-work and mesh system of markings, very suggestive of a cellular structure, distributed over the rest of the microsection, though the throwing a little out of focus of the microscopic field was neces-sitated in order to bring out clearly this system of markings, as Fig. 8, *b*, *c*, and Fig. 9, *a*, *b*, *c* will illustrate. The network stood out as light-colored markings and the meshes appeared as of a darker color, while a reversal of the focusing slightly beyond the point of sharp focus and in a direction toward the specimen gave the opposite color effect, though the contrast between the light and dark portions was less pronounced.[9] The cell walls of this net-work appear to cross the grain boundaries of the ferrite grains in places, thus indicating the presence of two distinct systems of etching patterns, the usual ferrite and pearlite system and the cellularlike system, the latter apparently being independent of and superposed on the former. This cellularlike structure was not developed in the case of the 0.008 and 0.030 per cent phosphorus B. O. H. steels even after fairly prolonged etching (20 to 25 minutes with 5 per cent alcoholic picric acid and 30 seconds with 2 per cent alcoholic nitric acid), though it was readily brought out in the

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[8] The author's attention was called, subsequent to the preparation of this paper, to G. F. Comstock's article "Microstructure of annealed soft steels, with special reference to phosphorus in tin plate," published in Forging and Heat Treatment, **7**, pp. 60–63, Jan., 1921, in which he reports the presence of faint relief markings in the ferrite areas comprising the "ghost streaks" in specimens of steel sheet bar containing 0.11 per cent carbon and 0.075 per cent phosphorus that had been annealed for four hours at 800 and 850° C., or within the Ac_1 to Ac_3 range, though this unusual structure was not shown as being present in specimens of the same steel annealed at 900° C. and at higher temperatures. On etching with Stead's reagent portions of this relief structure were darkened while the rest of the ferrite remained bright, thus indicating that phosphorus was responsible for this peculiar structure. Although it is true that the specimens used in this investigation were heated to 900° C, it would seem from the fact that the cellularlike structure persisted in many of the specimens examined that the time of heating to and above Ac_3 was not long enough to produce a complete diffusion of the phosphorus and consequent elimination of the relief or cellularlike structure. No attempt was made, however, to investigate this point fully, though the cellularlike structure was found to be more pronounced in the rapidly cooled specimens than in the slowly cooled ones.

[9] This color contrast as occasioned by the unequal depth of etching produced is in agreement with F. Osmond's observation, as stated on p. 17 of his Microscopic Analysis of Metals, edited by J. E. Stead and published by Charles Griffin & Co. (Ltd.), London, 1904, that cementite particles assume a dark color as contradistinguished with the light-colored ferrite background when the focusing of the microscope is carried toward the specimen and not quite to the point of focus. The network of the above-described cellularlike structure represents the portion of the metal which is lower in phosphorus content, as will be shown in a later section, and hence has been eaten away to a greater extent by the etching medium than the adjoining higher-phosphorus portions which stand out in relief.
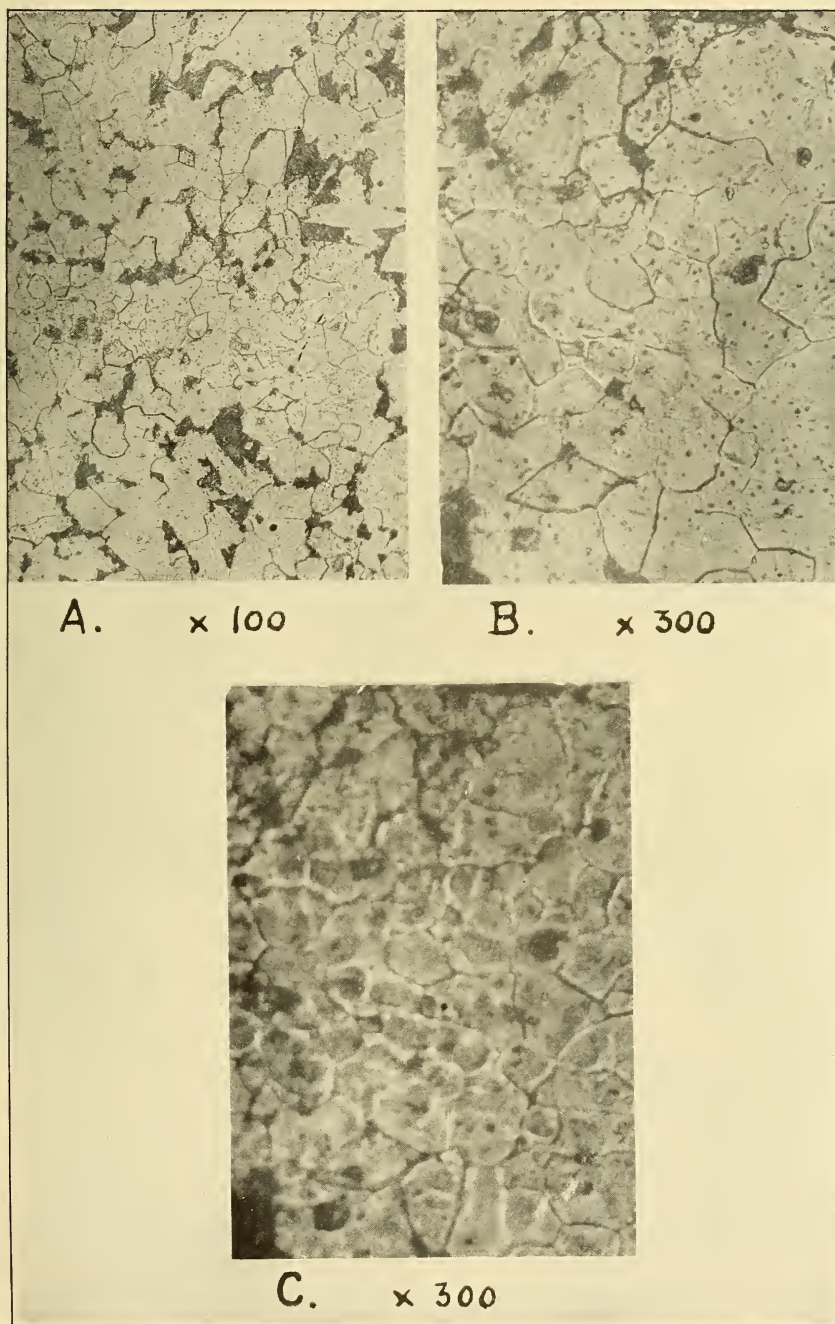
FIG. 8.—*Cellularlike structure in low-carbon acid open-hearth steel containing 0.032 per cent phosphorus*

Heated to 900° C and cooled through 750–600° C in 15 minutes. B was taken near center of field shown in A, and field is in sharp focus. C is same field as in B, but thrown a little out of focus to bring out cellularlike structure. Etching reagent, 5 per cent alcoholic solution of picric acid.
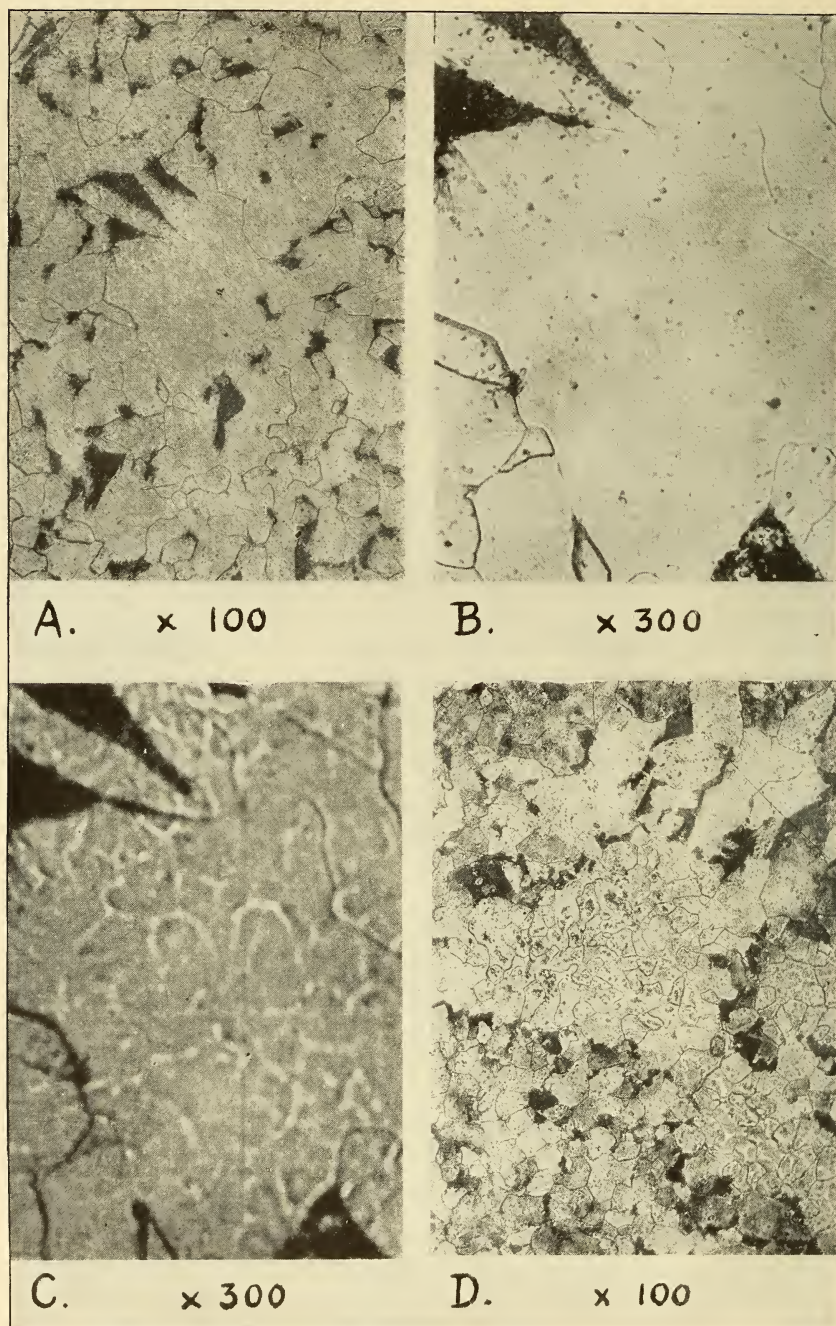
FIG. 9.—*Cellularlike structure in same specimen shown in Fig. 8 but at a different portion of microsection*

B was taken at center of field shown in A, and the field is in sharp focus. C is the same field as in B, but thrown a little out of focus to bring out cellularlike structure. D was taken at another spot in same microsection. Etching reagent, 5 per cent alcoholic solution of picric acid; D was also etched with Stead's reagent following the picric acid etching.

0.032 per cent phosphorus A. O. H. steel and in the other steels, both B. O. H. and A. O. H., containing the higher percentages of phosphorus. This fact suggests that the cellularlike structure will not be developed unless the phosphorus content of the steel be greater than about 0.01 or 0.02 per cent.

In order to prove that the carbonless areas, large ferrite grains, and cellularlike structure were due to the phosphorus, etching with alcoholic cupric chloride solution acidified with hydrochloric acid (Stead's reagent), which was found by trial to give more satisfactory results than several of the usual reagents recommended for the detection of phosphorus segregation such as Heyn's reagent, Rosenhain and Haughton's reagent, Stead's aqueous solution of picric acid, and heat tinting, was tried following the etching with picric acid or nitric acid. It is well known that through the action of Stead's reagent the portions of the etched surface low in phosphorus content have a layer of metallic copper or a brown-colored layer deposited thereon while the portions richer in phosphorus remain colorless or nearly so because of the greater resistance to the action of the etching.[10, 11, 12] As to the nature of the brown-colored deposit, Rawdon[13] states that this coloration or tint, attributed by Stead to a much-retarded deposition of copper, as represented by the darkened surface layer when dissolved off from the etched specimen gave a faint yet clear test for copper. In no case where etching with Stead's reagent was used in this work was there any metallic deposit of copper formed on the specimens.

Fig. 9, *d*, and Fig. 10, *a, b, c*, are typical of the results obtained by etching with Stead's reagent. It will be noted that the large carbonless areas and large individual ferrite grains remain practically colorless while the surrounding areas assume a mottled appearance, which on closer examination and at higher magnification was seen to possess a similar though less pronounced etch pattern as that developed in the 0.42 per cent phosphorus steel specimens described in the next subsection. However, in the case of the lower phosphorus steels (0.008 and 0.030 per cent phosphorus B. O. H.) the etch pattern was not very pronounced or definite, evidently because of the insufficient amount of phosphorus present.

[10] Stead, "Some of the ternary alloys of iron, carbon, and phosphorus," Jour. Soc. Chem. Ind., **33**, p. 174, 1914; seventh section of Part I; also Jour. Iron and Steel Inst., **91**, p. 174, 1915, I.

[11] Rawdon, "Some unusual features in the microstructure of wrought iron," Trans. Amer. Inst. Mining Engrs., **588**, p. 501, 1918; also B. S. Technologic Paper No. 97.

[12] Whiteley, "The distribution of phosphorus in steel between the points Ac_1 and Ac_3," Jour. Iron and Steel Inst., **101**, pp. 363 and 370–372; 1920, I.
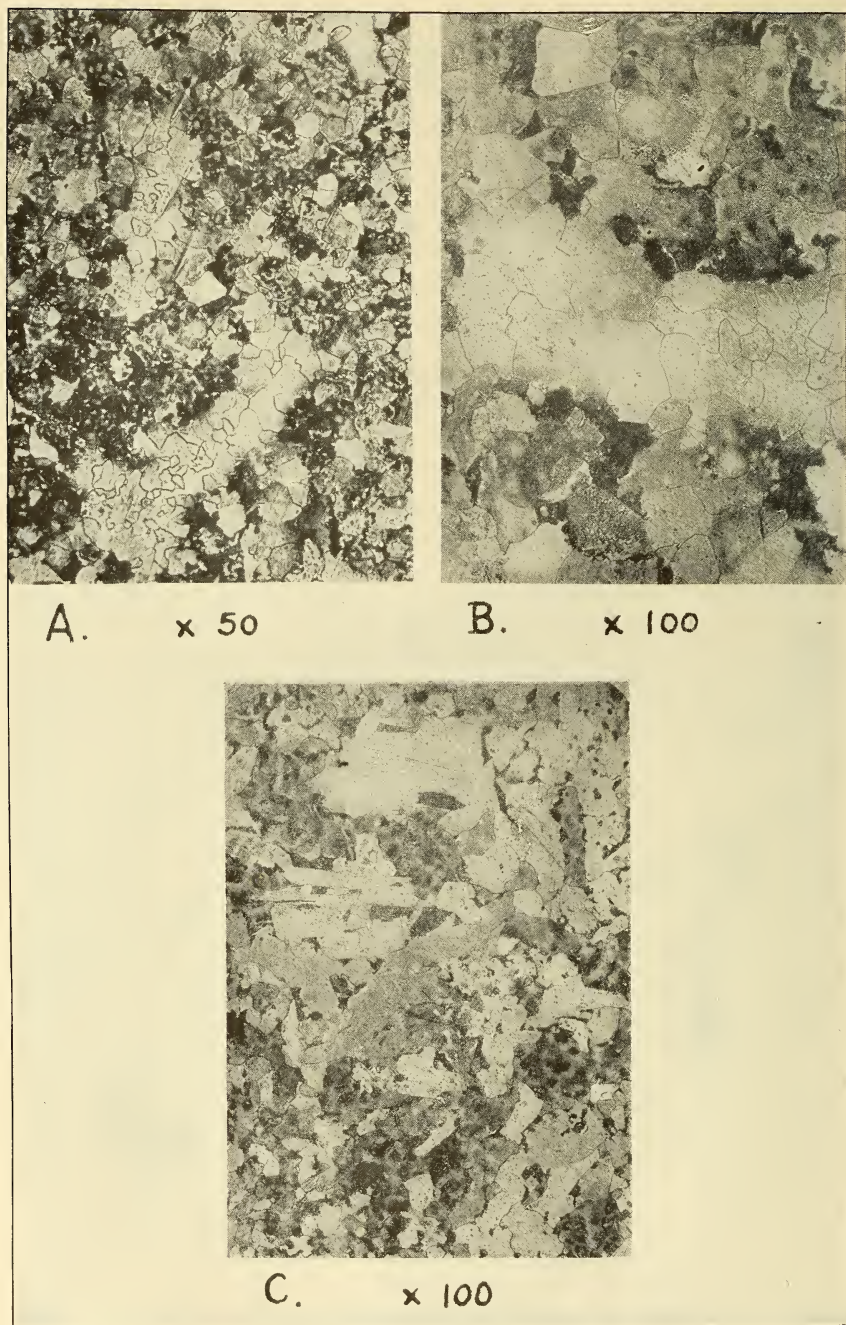
[13] See footnote 11.

FIG. 10.—*Carbonless areas and large ferrite grains in low-carbon acid open-hearth steel, as brought out by etching with Stead's reagent*

The specimen represented by A and B contained 0.032 per cent phosphorus, and was heated to 900° C and cooled through 750–600° C range in 2 hours. The specimen represented by C contained 0.058 per cent phosphorus, and was heated to 900° C and cooled through 750–600° range in 5 minutes. B was taken in the same microsection as A but at a different spot. Etching reagent, 5 per cent alcoholic solution of picric acid followed by Stead's reagent.

2. STEELS WITH HIGHER PHOSPHORUS CONTENT

For the purpose of determining whether or not a similar and more pronounced cellularlike structure as developed by etching with either picric or nitric acid and etching pattern as formed by Stead's reagent would be obtained in steels of higher phosphorus content, a series of specimens cut from a three-fourths-inch round of the following composition: 0.34 per cent carbon, 0.42 per cent phosphorus, 0.10 per cent silicon, 0.11 per cent manganese, and 0.029 per cent sulphur that had in connection with another investigation been heated to both 900 and 800° C and cooled through the 800 to 650° C range at various rates (two hours, one hour, accelerated furnace cooled, and air cooled) were studied.

A cellularlike structure similar to that found in the lower phosphorus steels was found present in the two-hour and one-hour cooled specimens of both the 900 and 800° C heatings (see Fig. 11 and Fig. 12, *a*, *b*) and in the accelerated furnace-cooled and air-cooled specimens of the 800° C heating, though in these last two specimens this cellularlike structure was quite clearly seen only at higher magnification because of the much finer granular structure (ferrite and pearlite) developed by the quicker rates of cooling. It should be noted that this cellularlike structure is absent in different spots where there is a cluster of more or less large pearlite kernels, and this is apparently due to a lower phosphorus content occasioned by the repellant action which carbon dissolved in iron is known to exert upon phosphorus. This assumption appears to be borne out in Fig. 13, *b*, and Fig. 15, *c*, where the areas surrounding the pearlite kernels have been deeply tinted by Stead's reagent, thus indicating a lower phosphorus content in these regions.

As for the results obtained by etching with Stead's reagent, Fig. 13, *a*, *c* show the general manner of distribution of the phosphorus as found in the two-hour and one-hour cooled specimens, the uncolored or light portions being richer in phosphorus than the dark portions. Figs. 12, *c*, and 13, *b* show in greater detail the arrangement of the low (dark) and high phosphorus (light) areas. The phosphorus-rich areas shown in Fig. 13, *a*, *c* appear to be the originally landlocked portions that had formed between the dendrites of purer iron or primary crystallites during the solidification of the metal, though the dendritic structure is not very marked evidently because of the working given the metal during its fabrication into three-fourths-inch rounds. It appears
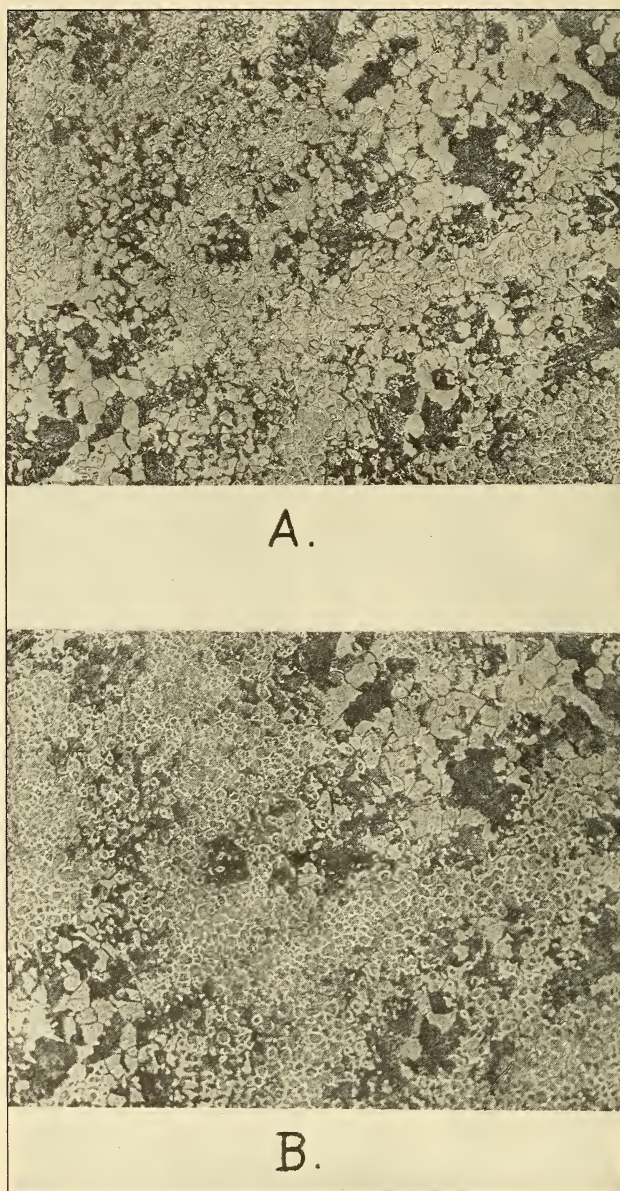
FIG. 11.—*Cellularlike structure in medium carbon steel containing 0.42 per cent phosphorus.* ×100

Heated to 900° C and cooled through 800–650° C range in 1 hour. B is same field as shown in A, but thrown a little out of focus. Etching reagent, 5 per cent alcoholic solution of picric acid.
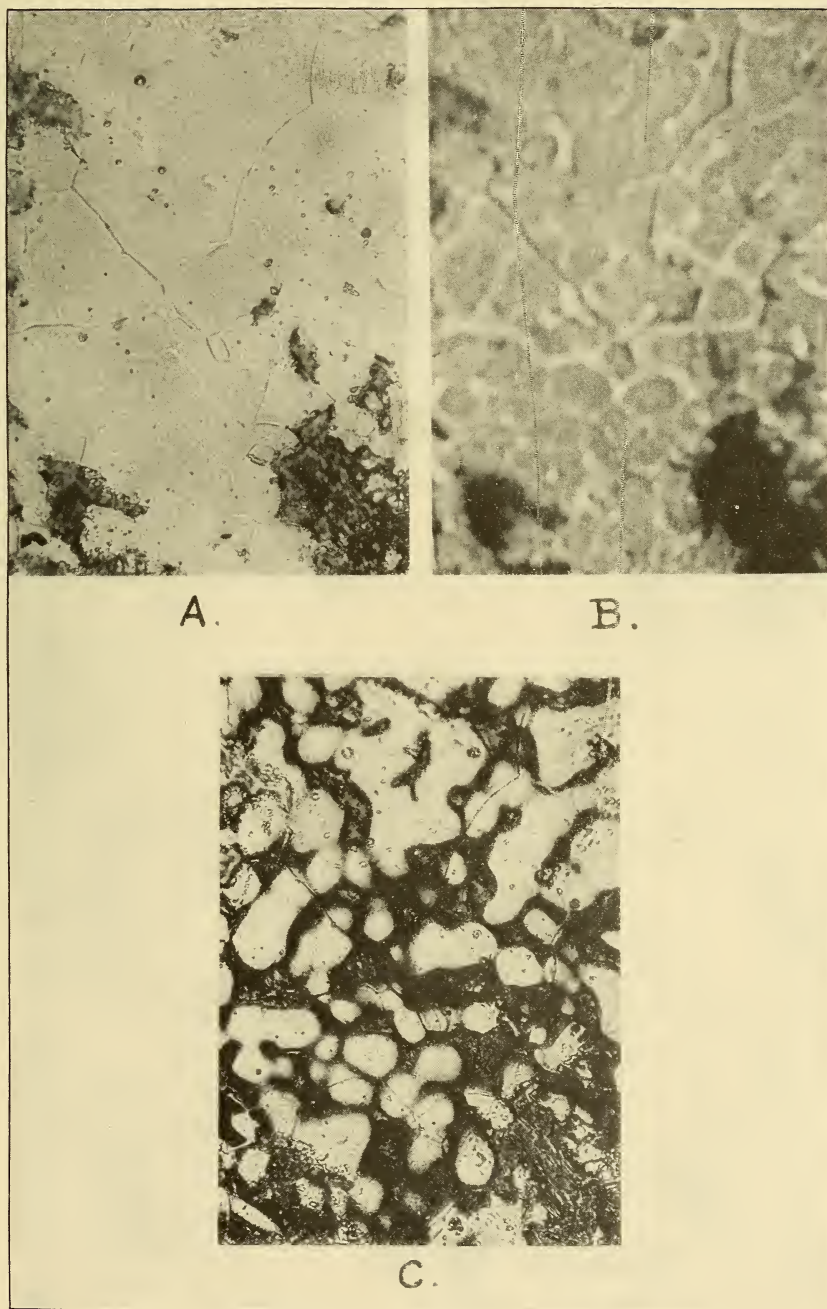
FIG. 12.—*Cellularlike structure in medium carbon steel containing 0.42 per cent phosphorus, before and after etching with Stead's reagent.* ×500

Same specimen as in Fig. 11, but taken at different portion of microsection. A, B, and C are of the same field, but B has been thrown a little out of focus. Etching reagent, 5 per cent alcoholic solution of picric acid; C was etched with Stead's reagent following the picric acid etching.
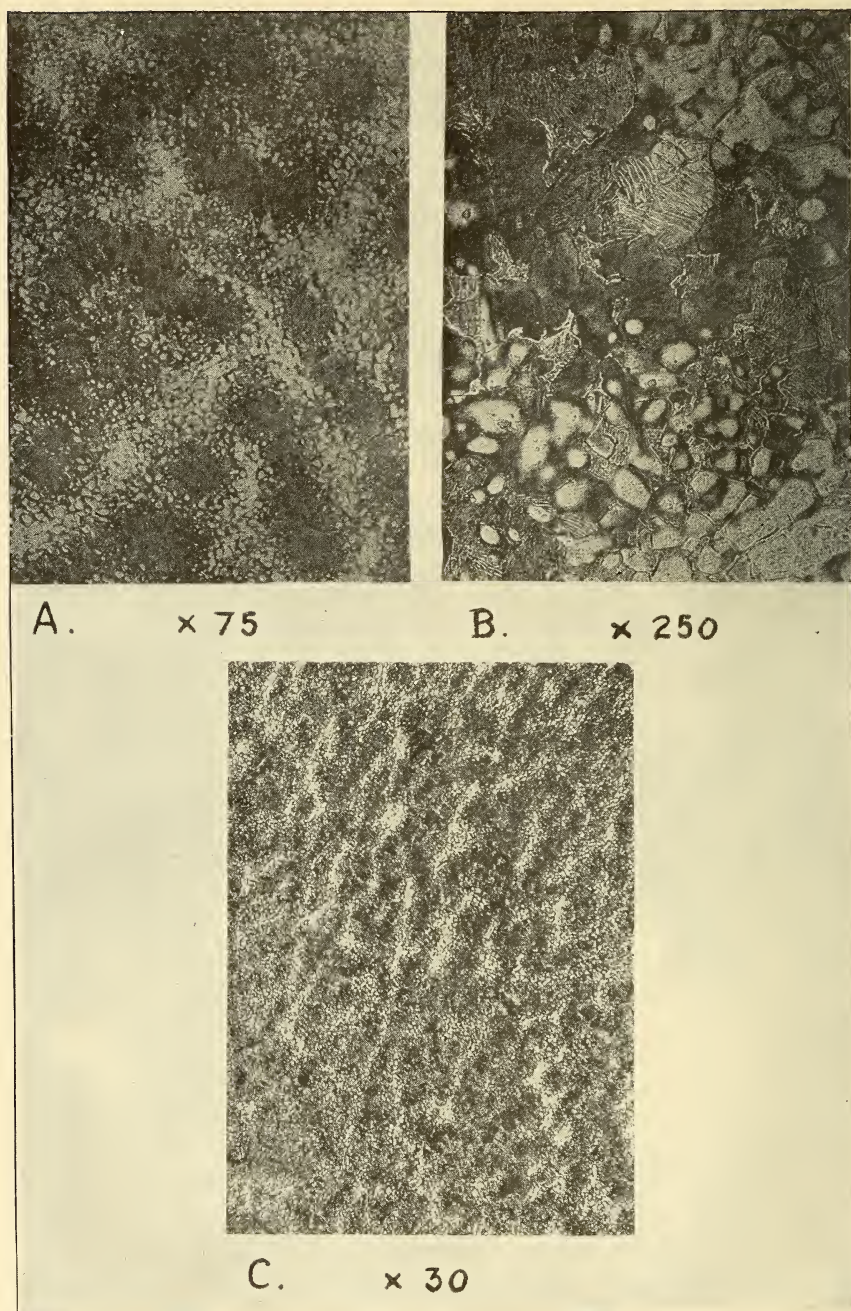
FIG. 13.—*Distribution of phosphorus (light areas) in medium carbon steel containing 0.42 per cent phosphorus, as revealed by etching with Stead's reagent*

The specimen represented by A and B was heated to 900° C and cooled through the 800–650° C range in 1 hour (same specimen as in Figs. 11 and 12), and that by C was heated to 900° C and cooled through 800–650° C range in 2 hours. B was taken at center of field shown in A. Etching reagents: A and B, 5 per cent alcoholic solution of picric acid followed by Stead's reagent; C, 2 per cent alcoholic solution of nitric acid followed by Stead's reagent.

probable that after the solidification had been completed the carbon diffused into the purer portions or the dendritic spines, leaving the other impurities as phosphorus and sulphur in the less pure portions or the landlocked areas as may be well illustrated in Fig. 7, *c*, where the carbon in the form of pearlite lies outside of a good-sized zone free from pearlite and containing numerous inclusions of manganese sulphide (cross-sectional view of the 1-inch round).

In the accelerated furnace-cooled and air-cooled specimens of the 900° C heating the phosphorus was found to be distributed in a different manner, as indicated in Fig. 14, *a*, and the phosphorus-rich portions (phosphoferrite or a solution of iron phosphide in iron) to be in the form of small acicular and globular-shaped masses grouped together in clusters, as shown in Figs. 14, *b*, *c* and 15, *c*. Fig. 15, *a*, *b* cover the same field as that in Fig. 15, *c*, but show the microsection as etched with nitric acid alone, thus revealing a light-colored etching pattern which corresponds exactly with the dark or low phosphorus portions of the etch pattern in Fig. 15, *c*.

It will also be noticed that the light-colored cell walls of the cellularlike structure in Fig. 12, *b* correspond exactly in position with and overlap the dark-colored etch-pattern in Fig. 12, *c*, though the latter is, in general, of greater width along the various cell walls. The light-colored network and dark-colored etch pattern are seen to cross the ferrite grain junctions in many places, and a similar tendency may be found in Fig. 13, *b*, thus confirming the statement made above (Sec. VI, 1) that the cellularlike structure appears to be independent of the ferrite and pearlite structure.

Fig. 14, *c* shows the structure of the 900° C air-cooled specimen, which had been heat tinted to a good blue color. The light-colored, phosphorus-rich portions stand out in good relief against the dark oxidized surface of the surrounding and poorer in phosphorus metal, and appear to be quite similar in general formation to that prevailing in the 900° C accelerated furnace-cooled specimen (Fig. 14, *b*). It may be of interest to note here Whiteley's statement[14] that areas containing as much as 0.6 per cent phosphorus are readily detected by heat tinting.

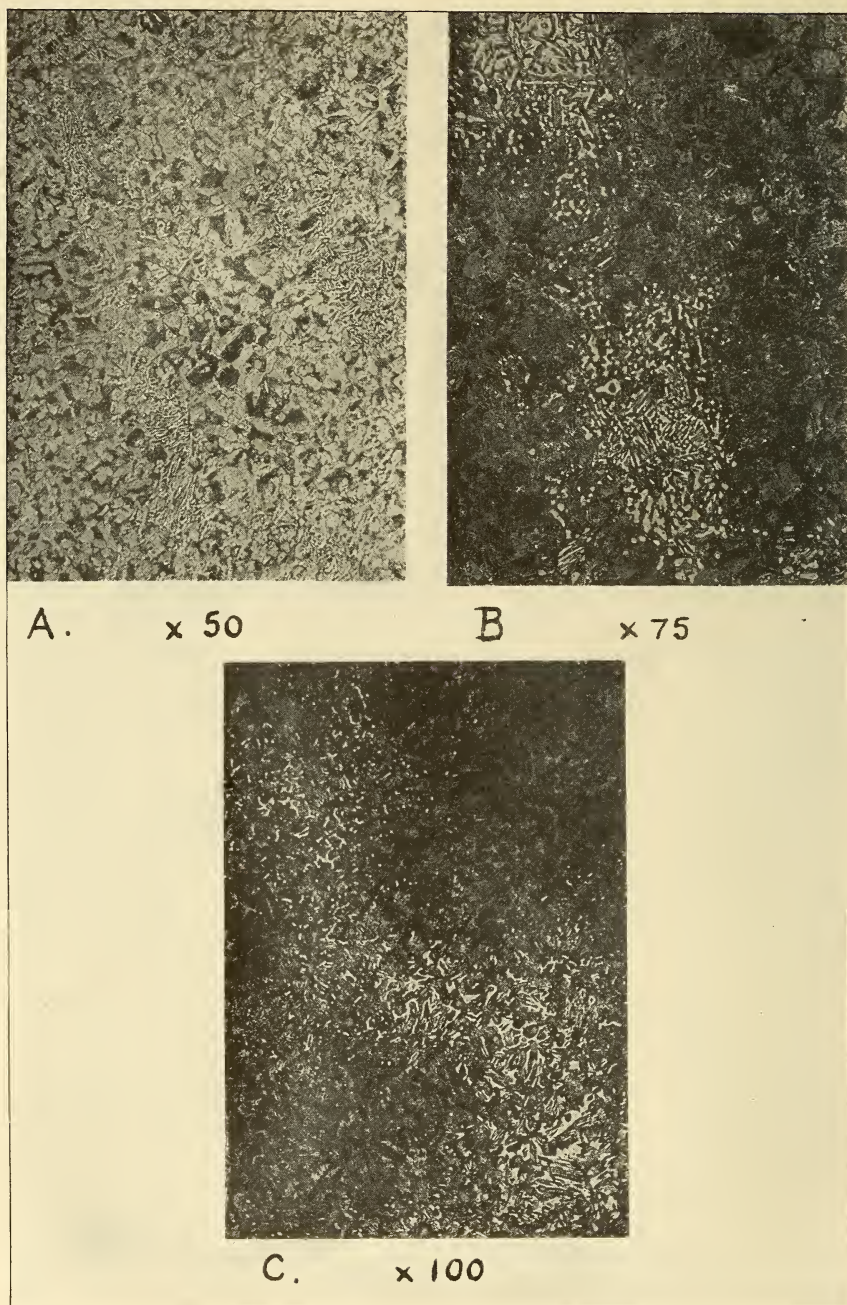[14] Loc. cit. (see footnote 12), p. 375.

FIG. 14.—*Distribution of phosphorus in medium carbon steel containing 0.42 per cent phosphorus*

The specimen represented by A and B was heated to 900° C and cooled quickly in the furnace, and that by C was heated to 900° C and air-cooled. Etching reagents: A, 2 per cent alcoholic solution of nitric acid; B, Stead's reagent; C, heat-tinted in molten lead bath at 300° C to good blue color.
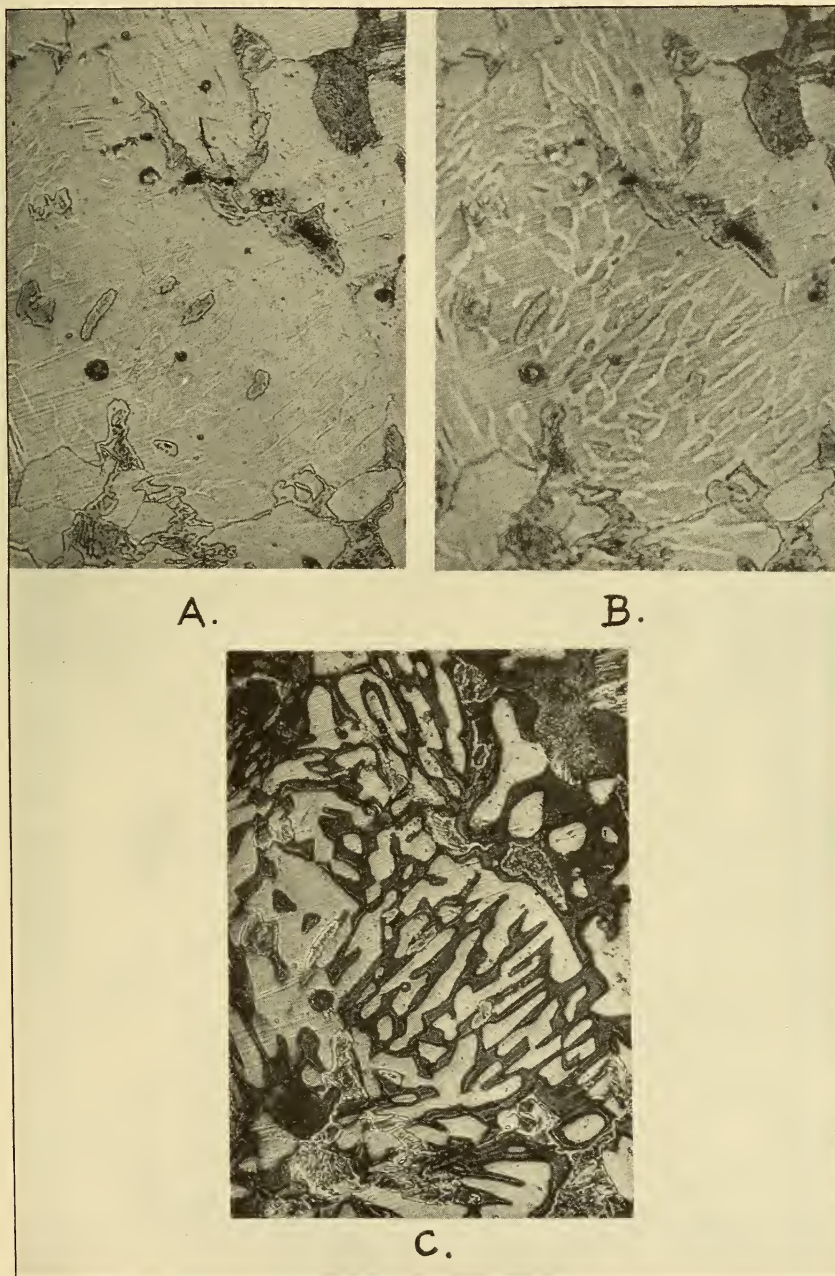
FIG. 15.—*Phosphorus-rich area shown in Fig. 14 (B), before and after etching with Stead's reagent.*   ×500

A, B, and C are of the same field, which was taken at center of the cluster of uncolored spots shown in lower half of Fig. 14 (B), though B has been thrown a little out of focus.   Etching reagent, 2 per cent alcoholic solution of nitric acid; C was etched with Stead's reagent following the nitric-acid etching.

3. INTERPRETATION OF RESULTS

It must be evident from the fact that the etch pattern as developed by Stead's reagent corresponds exactly in position with and overlaps the cellularlike structure as developed by picric or nitric acid etching that both systems of etch patterns are due to one and the same cause, the presence of phosphorus. This element is found to be more concentrated in the meshes of both etch patterns, these meshes appearing as dark areas in the cellularlike structure and as light areas in the etch pattern produced by Stead's reagent. This conclusion appears to be further borne out by the following considerations:

(*a*) Both the cellularlike structure and Stead's reagent etch pattern are more pronounced in the higher phosphorus steels than in the lower phosphorus steels.

(*b*) The large uncolored areas or meshes of the Stead's reagent etch pattern tend to be further away than nearer to the pearlite kernels or clusters of pearlite kernels in the 0.42 per cent phosphorus steel specimens, and a similar tendency has been observed to be present in the lower phosphorus steels, though in a less striking manner. This phenomenon is attributed to the repellant action of carbon upon phosphorus when in solution in the iron.

(*c*) In Figs. 13, *b* and 15, *c* it will be noted that the cementite laminæ of the pearlite kernels remain uncolored while the ferrite laminæ have been colored by etching with Stead's reagent. This fact proves that the cementite was little affected by the action of the etching medium and consequently remained uncolored or relatively so. It is reasonable to expect that iron phosphide or solid solution of phosphorus in iron would behave in a similar manner and consequently remain uncolored after etching with Stead's reagent, as has been pointed out by Stead[15] to be the case.

(*d*) Whiteley[16] states that a cellular structure which he was able to develop in his low-carbon steel specimens was due to the phosphorus, this structure becoming more pronounced as the percentage of phosphorus is increased, and he offers the explanation of the formation of this cellular structure as being due to the absorption by gamma-iron of ferrite richer in phosphorus during the slow heating of the specimens up to temperatures above 815° C.

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[15] Stead, "Iron, carbon, and phosphorus," Jour. Iron and Steel Inst., 1915, I, p. 140.
[16] Loc. cit. (see footnote 12), p. 377.

VII. SUMMARY AND CONCLUSIONS

1. Two series of specimens, one of basic open-hearth steel and the other of acid open-hearth steel, with the phosphorus content in each series varied in four or five steps within the limits 0.008 to 0.115 per cent, which mark the ordinary limits of phosphorus content in plain carbon steel, were employed in the study of the relationship between the phosphorus content and the microstructure and hardness resulting from a series of different heat treatments tried.

2. Marked irregularity in the distribution and grain size of both the ferrite grains and pearlite kernels was found present in many of the specimens, particularly in the acid open-hearth steel series. However, no definite relationship could be established between this irregularity of structure and grain size and the phosphorus content and also the heat treatment.

3. No well-defined relationship could be established between the phosphorus content and the scleroscope hardness, though somewhat more satisfactory results were obtained for the Brinell hardness. Despite some irregularity in the results, there is a small but definite increase in Brinell hardness as the phosphorus content is raised.

4. The irregularity in the microstructure as mentioned in paragraph 2 was traced to the nonuniform distribution of the phosphorus in the steel.

5. In addition to the microstructure as developed for these steels, a cellularlike etch pattern was formed in conjunction with and apparently superposed upon the ferrite and pearlite structure. Relationship between this cellularlike structure and the distribution of the phosphorus content was established.

Acknowledgment is made to Dr. Henry M. Howe, at whose suggestion this investigation was undertaken, for suggestions concerning the outline of the experimental procedure followed in the work, the use of his laboratory apparatus, and also the set of phosphorus steel samples which had been furnished him by Dr. Unger as stated in the Introduction.

WASHINGTON, May 20, 1921.